

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 829 312 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
04.06.2003 Bulletin 2003/23

(51) Int Cl.7: **B08B 7/00**, B08B 3/08,  
H01L 21/306

(21) Application number: **97305628.6**

(22) Date of filing: **25.07.1997**

**(54) Improvements in or relating to semiconductor devices**

Verbesserungen an oder in Bezug auf Halbleiteranordnungen

Améliorations aux ou relatives aux dispositifs semi-conducteurs

(84) Designated Contracting States:  
**DE FR GB IT NL**

(30) Priority: **25.07.1996 US 22811 P**

(43) Date of publication of application:  
**18.03.1998 Bulletin 1998/12**

(73) Proprietor: **TEXAS INSTRUMENTS  
INCORPORATED**  
**Dallas Texas 75265 (US)**

(72) Inventors:  
• **Douglas, Monte A.**  
**Coppell, Texas 75019 (US)**

• **Templeton, Allen C.**  
**Paris, Texas 75462 (US)**

(74) Representative: **Darby, David Thomas et al**  
**Abel & Imray,**  
**20 Red Lion Street**  
**London WC1R 4PQ (GB)**

(56) References cited:  
**EP-A- 0 391 035** **US-A- 5 105 556**  
**US-A- 5 352 327** **US-A- 5 356 538**

• **PATENT ABSTRACTS OF JAPAN vol. 13, no. 507**  
**(E-845), 14 November 1989 (1989-11-14) & JP 01**  
**204427 A (HITACHI LTD), 17 August 1989**  
**(1989-08-17)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 829 312 B1**

## Description

[0001] The instant invention pertains to semiconductor device fabrication and processing and more specifically to the removal of inorganic contamination at the surface of a semiconductor structure.

## BACKGROUND OF THE INVENTION

[0002] In the manufacture of, for example, integrated circuits and liquid crystal displays, contamination of the substrate and subsequent semiconductor layers causes many problems and should be reduced as much as possible. Examples of such contamination are residual particulates, organics, and metals. In addition, contaminants may be situated on the surface of the semiconductor layer, or they may be situated between the semiconductor layer and another layer (e.g. an oxide layer). Typically, wet-processing is utilized in the fabrication of semiconductor devices. A wet cleaning process may consist of a sequence of particle removal and metal removal steps, with a rinsing step performed between them, and concluding with a drying step. Drying is typically accomplished either by spinning the wafer so that the liquid on the wafer will be spun off or by raising the wafers from a cloud of hot isopropyl alcohol vapor which condenses on the surface of the wafer and displaces the water.

[0003] This type of wet cleaning process suffers from a particularly serious drawback, specifically, most metal removal processes of this type (typically consisting of strongly acidic mixtures) add particles to the surface of the wafer, and particle removal processes (typically comprised of basic/oxidant mixtures) add metals to the surface of the wafer. In addition, most wet cleaning processes suffer from the problems of: expense of obtaining electronic-grade wet chemicals; expense of disposing of the caustic chemicals which are used in wet cleaning processes; liquid surface tension limiting or preventing access of wet chemical cleaning to high aspect ratio features, like trenches; and lack of harmonization with all dry processing (which is utilized more frequently in semiconductor processing). Hence, a metal removal step followed by a particle removal step will result in residual metals, while the reverse process results in fewer particles but can become contaminated with metals by the final rinsing.

[0004] Supercritical fluids (namely, supercritical carbon dioxide) have received much attention, lately. This is especially true in the area's involving decaffeination of coffee and linen/fine clothing dry cleaning. In addition, supercritical CO<sub>2</sub> can be used in the removal of organic contaminants from semiconductor wafers. See International Journal of Environmentally Conscious Design & Manufacturing, Vol. 2, p. 83 (1993) (stating "supercritical carbon dioxide is best applied to the removal of organic compounds with mid-to-low volatilities"). However, supercritical CO<sub>2</sub> is generally regarded as ineffective in

cleaning inorganic contaminants (namely, metals) from semiconductor wafers.

[0005] EP 0 391 035 A2 describes a method of removing undesired contaminants from a substrate by exposing the substrate to ultraviolet radiation and a particular dense fluid simultaneously. The dense fluids suitable for use comprise supercritical or liquefied gases, or inorganic liquids at standard temperature and pressure. The fluid chosen is selected to have a solubility chemistry similar to that of the targeted contaminant. The particular frequency of UV radiation is also selected and the preferred range is 184-300 nm. The dense fluid bathes the substrate surface and dissolves or suspends the contaminants so that they can be dissociated by the UV radiation. The dense fluid also suspends and transports the dissociated products, thereby enhancing the removal of the contaminants.

[0006] In JP 01204427, a substrate is located in a cleaning bath and the substrate is brought into contact with a supercritical gas in which a third component is incorporated. Contaminations can thus be removed from the substrate. This is particularly useful for obtaining an excellent quality semiconductor whose minimum machining size is 0.3µm or less.

[0007] Relating to another field, a group of researchers have discovered a way of removing metals from vegetation by subjecting the vegetation to supercritical CO<sub>2</sub> and neutralizing the metals with chelating agents. See Elizabeth K. Wilson, Toxic Metals Extracted with Supercritical Carbon Dioxide, C&EN 27 (April 15, 1996). However, this work states that "by itself, nonpolar supercritical CO<sub>2</sub> is almost useless for solvating positively charged heavy-metal ions. However, researchers; have discovered that metals can be solvated if they are first neutralized by chelating agents and, furthermore, that the solvency increases dramatically when the chelating agents are fluorinated." Id. at 27. However, there are several problems with this approach. First, there is a difficulty removing uncharged metals. Second, unfluorinated chelating agents are expensive. Third, mass scale synthesis of fluorinated chelating agents is expensive. Fourth, fluorinated and unfluorinated chelating agents are highly toxic and expensive to purify and dispose of. Fifth, there is a limited range of metals that can be readily solvated by the fluorinated chelating agents. Sixth, diffusion of unchelated metals into an underlying semiconductor substrate would be disastrous using the methodology of this publication.

[0008] US Patent no. 5,356,538 describes a method of cleaning soil of metalloid and metal contamination by exposing the contaminated material to a supercritical fluid solvent containing a chelating agent, e.g. ionizable crown ethers, such as crown ether carboxylic acids.

[0009] It is an object of the instant invention to provide a method of removing metal contaminants from semiconductor wafers. It is another object of the instant invention to provide a method of removing inorganic contaminants from semiconductor wafers.

## SUMMARY OF THE INVENTION

[0010] In summary, one embodiment of the instant invention is a method which overcomes the problems involved with chemical modification of the ionic and neutral, light and heavy inorganic (metal) species and which renders these ionic and neutral, light and heavy inorganic (metal) species soluble upon exposure to conventional, inexpensive, high purity, nontoxic solvents. The method of the instant invention includes the steps of chemically altering the metal (inorganic) contaminants on the surface of the native oxide (which overlies the semiconductor substrate). This is preferably accomplished using a very broad spectrum of modification agents/chemicals, and the metal alteration may occur before or during exposure to a supercritical fluid (preferably CO<sub>2</sub>). Next, the chemically-altered metal is exposed to a conventional solvent incorporated within a supercritical CO<sub>2</sub> fluid. Finally, the conventionally-solvated, chemically-altered metal is removed in the supercritical CO<sub>2</sub> medium. Key aspects of this invention are that the inorganic contaminant is not soluble in the supercritical CO<sub>2</sub> fluid without prior chemical alteration, and the chemically-altered inorganic contaminant may be removed by the solvent simultaneously with the chemical alteration step.

[0011] An embodiment of the instant invention is a method of removing inorganic contamination from a surface of a semiconductor substrate, said method comprising the steps of: reacting the inorganic contamination having a first solubility in at least one solvent agent with at least one conversion agent to convert said inorganic contamination into a converted inorganic contamination which has a second solubility in said at least one solvent agent; removing said converted inorganic contamination having said second solubility in said at least one solvent agent by subjecting it to said at least one solvent agent, said solvent agent being included in a first supercritical fluid (preferably supercritical CO<sub>2</sub>); wherein said second solubility in said at least one solvent agent is greater than said first solubility in said at least one solvent agent. Preferably, the conversion agent is selected from the group consisting of: an acid agent, a basic agent, a chelating agent, a ligand agent, a halogen-containing agent, and any combination thereof. Preferably, the inorganic contamination is situated on substantially the surface of a native oxide which overlies the substrate, and it may consist of metal contamination. The conversion agent may be included in a second supercritical fluid, which is preferably supercritical CO<sub>2</sub>. The steps of reacting the inorganic contamination with at least one conversion agent and removing the converted inorganic contamination by subjecting it to at least one solvent agent may be performed simultaneously or sequentially. Preferably, the solvent agent is selected from the group consisting of: a polar gas, a nonpolar gas, a polar supercritical fluid, a nonpolar supercritical fluid, a polar species, a nonpolar species, a surfactants,

a detergent, a amphoteric material, or a chelating agent.

[0012] Another embodiment of the instant invention is a method of removing metallic contamination from a surface of a semiconductor substrate, said method comprising the steps of: reacting the metallic contamination having a first solubility in at least one solvent agent with at least one conversion agent to convert said metallic contamination into a converted metallic contamination which has a second solubility in said at least one solvent agent, the conversion agent being included in a first supercritical CO<sub>2</sub> fluid; removing said converted metallic contamination having said second solubility in said at least one solvent agent by subjecting it to said at least one solvent agent, the solvent agent being included in a second supercritical CO<sub>2</sub> fluid; wherein said second solubility in said at least one solvent agent is greater than said first solubility in said at least one solvent agent and wherein the reacting step and the removing step are performed sequentially.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The present invention will now be further described, by way of example, with reference to the accompanying drawing in which:-

FIGURE 1 is a schematic drawing of a sample cleaning system in accordance with an embodiment of the instant invention.

## DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0014] FIGURE 1 illustrates a process system which can be utilized to implement the method of the instant invention. The sample to be cleaned (the semiconductor wafer with inorganic contamination present) is held in container 16. A supercritical fluid (preferably a CO<sub>2</sub> gas) is supplied from a gas reservoir 28 which is connected by a conduit 30, which includes valve 32, to a pressurization unit 34 that increases the pressure on the gas to greater than approximately 70 to 75 atmospheres at a temperature greater than approximately 32°C to form the supercritical fluid. The supercritical fluid (SCF) travels through valve 36 and conduit 38 to a reservoir 12 (as long as valves 1 and 3 are open and valve 2 is closed) that holds a solid, liquid, or gas modification agent(s). Possible modification agents are listed below. The passing of the SCF through the modification agent acts to incorporate the modification agent into the SCF. The SCF incorporated with the modification agent to leave reservoir 12 and enter container 16. The SCF mixture and inorganic contamination are introduced, resulting in the modification of the inorganic contamination.

[0015] Subsequent to or simultaneous with modification of the inorganic contamination on the semiconductor sample by the modification agent, the SCF travels through valve 36 and conduit 38 to reservoir 14 which

holds a solid, liquid, or gaseous solvent agent(s). This is accomplished by closing valves 1, 3, and 5 and opening valves 2, 4, and 6. The passing of the SCF through the solvent agent acts to incorporate the solvent agent into the SCF. The SCF incorporated with the solvent agent leaves reservoir 14 and enters chamber 16. The SCF mixture and modified inorganic contamination are introduced, thereby resulting in the removal of the modified inorganic contamination from the surface of the sample (preferably a semiconductor wafer).

[0016] The modified inorganic contaminant and the CO<sub>2</sub> are removed and passed through depressurization valve 18 such that the inorganic contaminant precipitates in container 20. The CO<sub>2</sub> gas is then recycled by pump 24 through line 26 to reservoir 28. The inorganic contaminants can be removed via line 22.

[0017] One embodiment of the instant invention is a method of removing inorganic contamination (preferably metals) from the top monolayer of a conductive, semiconductive, or insulating layer. The "top monolayer" generally refers to the top 5μm of the layer, and the layer is generally comprised of an oxide (probably a native oxide layer).

[0018] In general, this embodiment of the instant invention is a method to remove inorganic contamination, including metals, from substrate surfaces or the surface of a native oxide, grown on the substrate, by chemical conversion of the inorganic material to a different material that has higher solubility in a solvent for subsequent removal by the solvent in a supercritical fluid (preferably supercritical CO<sub>2</sub>). More specifically, the method of this embodiment would preferably comprise the steps of: reacting the inorganic contamination with a conversion agent; and removing the converted inorganic contamination product with a solvent (which is preferably completely or partially contained within a supercritical fluid, such as CO<sub>2</sub>). The conversion agent may be an acid (preferably KCN, HF, HCl, or KI), a base (preferably NH<sub>4</sub>OH, KOH, or NF<sub>3</sub>), a chelating and/or ligand agent (preferably dibetaketone), or a halogen-containing agent (preferably CO, HN<sub>3</sub>, NO, COS, HN<sub>4</sub>OH, water, or H<sub>2</sub>O<sub>2</sub>). The conversion agent may be introduced to the semiconductor wafer by vapor exposure, plasma exposure, or incorporating the conversion agent in a supercritical fluid (preferably CO<sub>2</sub>) and exposing the wafer to this combination. The solvent may be comprised of a polar gas (preferably CO, COS, NO, NH<sub>3</sub>, or NF<sub>3</sub>), nonpolar gases (preferably N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, or F<sub>2</sub>), polar SCF (preferably NO<sub>2</sub>), nonpolar SCF (preferably CO<sub>2</sub>), a polar species (preferably water, ethanol, methanol, acetone, or glycol), a nonpolar species (preferably tetrahydrofuran, or dimethylformamide), surfactants, detergents, or amphoteric materials (preferably sodium dodecyl sulfate, quaternary ammonium salts, or cationic, anionic, nonionic or zwitterionic surfactants), or a chelating agent (preferably beta-diketone, fluorinated or unfluorinated crown ether).

[0019] Although specific embodiments of the present

invention are herein described, they are not to be construed as limiting the scope of the invention. The invention is to be limited only by the scope of the appended claims.

## Claims

1. A method of removing inorganic contamination from a surface of a semiconductor substrate, said method comprising the steps of:

reacting said inorganic contamination having a first solubility in at least one solvent agent with at least one conversion agent to convert said inorganic contamination into a converted inorganic contamination which has a second solubility in said at least one solvent agent; removing said converted inorganic contamination having said second solubility in said at least one solvent agent by subjecting it to said at least one solvent agent, said solvent agent being included in a first supercritical fluid;

wherein said second solubility in said at least one solvent agent is greater than said first solubility in said at least one solvent agent.

2. A method according to claim 1, wherein said conversion agent is selected from the group consisting of: an acid agent, a basic agent, a chelating agent, a ligand agent, a halogen-containing agent, and any combination thereof.
3. A method according to claim 1 or claim 2, wherein said first supercritical fluid is supercritical CO<sub>2</sub>.
4. A method according to any one of the preceding claims, wherein said inorganic contamination is situated on the surface of a native oxide which overlies said substrate.
5. A method according to any one of the preceding claims, wherein said conversion agent is included in a second supercritical fluid.
6. A method according to claim 5, wherein said second supercritical fluid is supercritical CO<sub>2</sub>.
7. A method according to any one of the preceding claims, wherein said steps of reacting said inorganic contamination with said at least one conversion agent and removing said converted inorganic contamination by subjecting it to said at least one solvent agent are performed simultaneously.
8. A method according to any one of the preceding claims, wherein said solvent agent is selected from

the group consisting of: a polar gas, a nonpolar gas, a polar supercritical fluid, a nonpolar supercritical fluid, a polar species, a nonpolar species, a surfactant, a detergent, an amphoteric material and a chelating agent.

9. A method according to any one of the preceding claims, wherein said inorganic contamination is metal contamination.

#### Patentansprüche

1. Verfahren zum Entfernen einer anorganischen Verunreinigung von einer Oberfläche eines Halbleitersubstrats mit den Schritten:

Umsetzen der anorganischen Verunreinigung, die eine erste Löslichkeit in mindestens einem Lösungsmittel aufweist, mit mindestens einem Umwandlungsmittel zum Umwandeln der anorganischen Verunreinigung in eine umgewandelte anorganische Verunreinigung, die in dem mindestens einen Lösungsmittel eine zweite Löslichkeit aufweist,

Entfernen der umgewandelten anorganischen Verunreinigung mit der zweiten Löslichkeit in dem mindestens einen Lösungsmittel, indem sie dem mindestens einen Lösungsmittel ausgesetzt wird, wobei das Lösungsmittel in einem ersten überkritischen Fluid enthalten ist,

wobei die zweite Löslichkeit in dem mindestens einen Lösungsmittel größer ist als die erste Löslichkeit in dem mindestens einen Lösungsmittel.

2. Verfahren nach Anspruch 1, wobei das Umwandlungsmittel aus der Gruppe ausgewählt wird, die aus einer Säure, einer Base, einem Komplexbildner, einem Ligandenmittel, einem halogenhaltigen Mittel und beliebigen Kombinationen von diesen besteht.
3. Verfahren nach Anspruch 1 oder 2, wobei das erste überkritische Fluid überkritisches CO<sub>2</sub> ist.
4. Verfahren nach einem der vorhergehenden Ansprüche, wobei sich die anorganische Verunreinigung auf der Oberfläche eines über dem Substrat liegenden nativen Oxids befindet.
5. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Umwandlungsmittel in einem zweiten überkritischen Fluid enthalten ist.
6. Verfahren nach Anspruch 5, wobei das zweite überkritische Fluid überkritisches CO<sub>2</sub> ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Schritte des Umsetzens der anorganischen Verunreinigung mit dem mindestens einen Umwandlungsmittel und des Entferns der umgewandelten anorganischen Verunreinigung, indem sie dem mindestens einen Lösungsmittel ausgesetzt wird, gleichzeitig ausgeführt werden.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Lösungsmittel aus der Gruppe ausgewählt wird, die aus einem polaren Gas, einem unpolaren Gas, einem polaren überkritischen Fluid, einem unpolaren überkritischen Fluid, einer polaren Spezies, einer unpolaren Spezies, einem oberflächenaktiven Mittel, einem Reinigungsmittel, einem amphoterischen Material und einem Komplexbildner besteht.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei die anorganische Verunreinigung eine Metallverunreinigung ist.

#### Revendications

1. Procédé d'élimination d'une contamination inorganique d'une surface d'un substrat semiconducteur, ledit procédé comprenant les étapes de :

mise en réaction de ladite contamination inorganique ayant une première solubilité dans au moins un agent solvant avec au moins un agent de conversion pour convertir ladite contamination inorganique en une contamination inorganique convertie qui a une seconde solubilité dans ledit au moins un agent solvant ;  
élimination de ladite contamination inorganique convertie ayant ladite seconde solubilité dans ledit au moins un agent solvant en la soumettant audit au moins un agent solvant, ledit agent solvant étant inclus dans un premier fluide supercritique;

dans lequel ladite seconde solubilité dans ledit au moins un agent solvant est supérieure à ladite première solubilité dans ledit au moins un agent solvant.

2. Procédé selon la revendication 1, dans lequel ledit agent de conversion est sélectionné parmi le groupe consistant en : un agent acide, un agent basique, un agent de chélation, un agent ligand, un agent contenant des halogènes, et une combinaison quelconque de ceux-ci.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel ledit premier fluide supercritique est du CO<sub>2</sub> supercritique.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite contamination inorganique est située sur la surface d'un oxyde natif qui recouvre ledit substrat. 5
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit agent de conversion est inclus dans un second fluide supercritique. 10
6. Procédé selon la revendication 5, dans lequel ledit second fluide supercritique est du CO<sub>2</sub> supercritique. 20
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel lesdites étapes de mise en réaction de ladite contamination inorganique avec ledit au moins un agent de conversion et d'élimination de ladite contamination inorganique convertie en la soumettant audit au moins un agent solvant, sont réalisées simultanément. 25
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit agent solvant est sélectionné parmi le groupe consistant en : un gaz polaire, un gaz non polaire, un fluide supercritique polaire, un fluide supercritique non polaire, une espèce polaire, une espèce non polaire, un agent tensioactif, un détergent, une matière amphotère et un agent de chélation. 30
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite contamination inorganique est une contamination métallique. 35

40

45

50

55

60

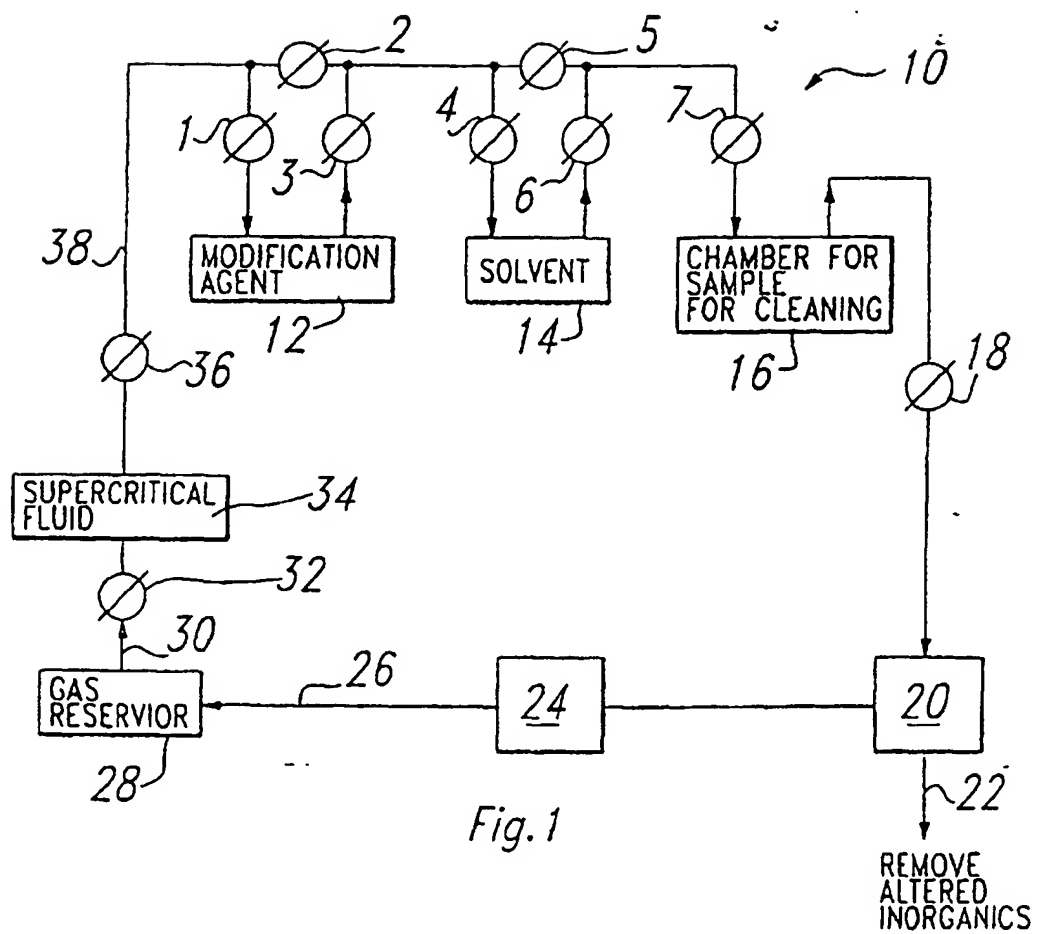


Fig. 1